

Minimum Voltage to Reduce Aluminum Oxide

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Minimum Voltage to Reduce Aluminum Oxide¹

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The specific heat of crystalline alumina has been determined by a method involving the diffusion of heat through a cylinder of the powdered material. The results of this determination have been combined with the thermodynamic properties of alumina as given in the literature to compute the minimum theoretical voltage required to reduce alumina to molten aluminum and gaseous oxygen. It is probable that this value is reduced in the commercial process by oxidation of the carbon anode. Making allowance for this reduction in potential, the theoretical minimum voltage at 950° C. is computed to be 0.947.

THE present commercial process for the production of metallic aluminum involves the electrolysis of a solution of aluminum oxide at temperatures between 900° and 1000° C. In view of the commercial importance of this process, it becomes of interest to calculate the minimum electrical energy which would be required if the process could be operated under ideal conditions. Commercially, mechanical conditions may outweigh energy efficiency, but such a calculation serves as a useful basis for comparison with actual operation.

The method of calculation used depends upon the third law of thermodynamics (11) and requires the following numerical data: (a) the absolute entropies of solid aluminum,

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gaseous oxygen at atmospheric pressure, and crystalline aluminum oxide; (b) the heat of formation of aluminum oxide from solid aluminum and gaseous oxygen; (c) the heat capacities of gaseous oxygen and of crystalline aluminum oxide, both as functions of temperature up to that of the commercial electrolytic process; (d) the heat capacity of solid aluminum from room temperature to the melting point; (e) the melting point of solid aluminum; (f) the latent heat of fusion of aluminum; (g) the heat capacity of liquid aluminum from the melting point up to the temperature of the commercial electrolytic process.

From these data one can calculate the thermodynamic potential (10) or "free energy" ($\Delta F = \Delta H - T \Delta S$) of formation (12) of aluminum oxide from aluminum and gaseous oxygen at any temperature within the range covered. Having a numerical value for the ΔF of formation at any temperature, the minimum electromotive force required for the decomposition of aluminum oxide into aluminum and oxygen at that temperature may be easily calculated from the equation $NFE = -\Delta F$. Furthermore, the equilibria between carbon, oxygen, carbon monoxide, and carbon dioxide at that temperature being known, the reduction of minimum electromotive force due to anode reactions can also be calculated.

In an attempt to assemble the necessary data for these calculations, it appeared that reliable results had been reported covering every item except the heat capacity of aluminum oxide from room temperature upward. For this reason the following experimental work was undertaken to obtain this necessary information.

Heat Capacity of Crystalline Aluminum Oxide

GENERAL DESCRIPTION OF THE METHOD—The method was a modification of the one proposed by Brown and Furnas (2). A common method of determining the heat capacity of a liquid is to apply a known quantity of heat to a known weight of the liquid by means of a submerged heating element, stirring the liquid before, during, and after heating. In this way, subject to suitable corrections, the uniform temperature rise is easily measured by means of a thermometer. In the case of a powdered solid the possibility of maintaining the powder at a uniform temperature by stirring does not exist. However, if a known weight of uniformly packed powder is heated by means of an internal heating element and if the temperature distribution throughout the mass is known before and after heating, the temperature rises throughout the mass may be integrated and the mean rise may be calculated, provided that no error is introduced by neglecting the heat escaping to the surroundings during a determination.

For practical purposes a cylindrical shell packed with the powder lends itself well to this method. Coaxial with the shell is placed a cylindrical heating element of small diameter. The cylinder ends are well insulated to minimize the axial

flow of heat. In a plane perpendicular to the axis of the cylinders and midway between the ends, the hot junctions of several thermocouples are placed at known radial distances from the axis. Thus the millivolt distribution can be read at any time and curves can be plotted showing millivolts as a function of time for each radial distance represented by a thermocouple. From these curves it is easy to read off a series of millivolt values for all couples at two different times and, by subtracting the two values thus found for each couple, to determine the millivolt rise or fall, for each radial distance, between the two times. If the characteristics of the thermocouple alloys are known, the millivolt rise in each case may be

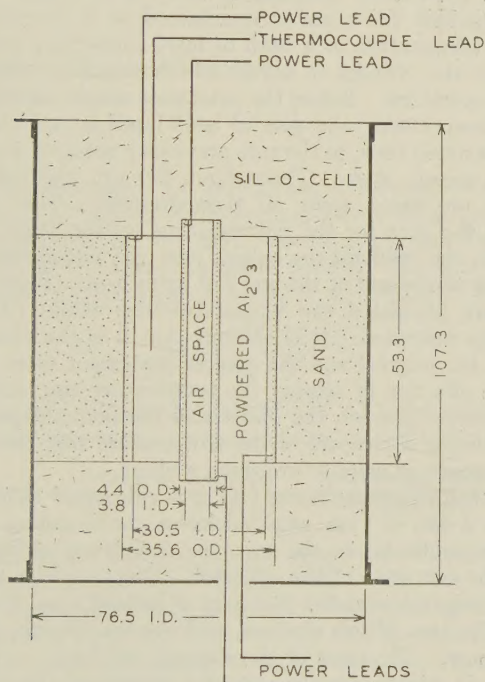


Figure 1—Apparatus for Determining Specific Heat of Alumina

multiplied by the known mean rate of change of temperature with millivoltage (dT/dE) over the millivolt range during the rise. This operation converts millivolt rise into temperature rise, on account of the justifiable assumption that, over a small range, $\Delta T/\Delta E = dT/dE$, and $\Delta T = \Delta E(dT/dE)$.

These temperature-rise values then require integration in order to determine the mean effective temperature rise during the known period of time.

The success of the method hinges upon the elimination of serious error due to heat losses to the surroundings during the period of measured heat input. This is accomplished by

the following procedure: Before beginning a determination, a constant energy input is maintained to the heating element until a "steady state" is reached, or, in other words, until there is no further change of temperature at any radius as time goes on. At this time the rate of heat loss to the surroundings is equal to the rate of heat input. Then the rate of heat input is suddenly increased at noted time and the new heat input carefully measured. The thermocouples nearest the axis will be the first affected by this wave of additional heat, but a considerable period of time will elapse before any change is noted in the couples farthest from the axis. As long as the temperature at the outermost couple remains unchanged, the rate of heat loss to the surroundings will not vary, provided the room is maintained at a substantially uniform temperature or a bath of inert conducting material surrounds the cylinder to act as a buffer against changes in room temperature. Before the outermost couple has shown a rise in temperature, the rate of heat input is suddenly reduced, at noted time, to the rate previously required to maintain the steady state. Throughout the run millivolt-time readings are taken from all thermocouples. This record provides the data for the millivolt-time curves, from which are taken the millivolt-rise values over the period from the beginning to the end of the wave of extra heat. From these values are calculated the temperature-rise values (ΔT) as previously indicated. It is obvious that it is the difference between the original and the greater heat-input rates which has been effective in causing the temperature rise, and that the difference between the initial and the final temperature distribution is a measure of the temperature rise, the intermediate readings merely furnishing a check.

The mean temperature rise (ΔT_m) is calculated as follows: Consider a disk of 1 cm. axial thickness, the bounding planes being perpendicular to the axis, the disk lying midway between the two ends of the cylinder. Then consider an element of this disk of radial thickness dr located r cm. from the axis. The area of this element, and also its volume, will be $V = 2\pi r.dr$. The mass of the element will be $m = DV = 2D\pi r.dr$, in which D is the apparent density of the powder. The heat absorbed in this element during any period of time will be the product of the specific heat, the mass, and the temperature rise, or

$$\text{Heat absorbed} = Cm\Delta T = 2CD\Delta T\pi r.dr$$

The total heat absorbed in the disk during any period of time will be found by integrating the above equation between the inside and outside radii of the powder-packed space. This gives

$$\text{Total heat absorbed} = 2\pi CD \int_{r_1}^{r_2} r \Delta T.dr$$

If the same amount of heat absorption had been applied in causing a uniform rise in temperature throughout the mass,

between the same two radii as above, ΔT would have been a constant and it could be taken from under the integral sign and called ΔT_m . This would have given

$$\text{Total heat absorbed} = 2\pi CD \Delta T_m \int_{r_1}^{r_2} r \cdot dr$$

As we are discussing the same total heat absorption in both cases, we may equate the two expressions for total heat absorbed, and solve the resulting equation for ΔT_m . This gives

$$\Delta T_m = \frac{\int_{r_1}^{r_2} \Delta T \cdot r \cdot dr}{\int_{r_1}^{r_2} r \cdot dr}$$

The numerator is identical with

$$\int_{r_1}^{r_2} r^2 \cdot \Delta T d \ln r = 2.3 \int_{r_1}^{r_2} r^2 \cdot \Delta T d \log r$$

This final expression for the numerator can be evaluated by plotting $r^2 \Delta T$ against corresponding values of $\log r$, ascertaining the area under the curve between $\log r_1$ and $\log r_2$, and multiplying the area thus found by 2.3. The denominator, on formal integration, gives $1/2(r_2^2 - r_1^2)$. Finally,

$$\Delta T_m = \frac{(2.3) (\text{area})}{1/2 (r_2^2 - r_1^2)}$$

Having obtained a numerical value of ΔT_m , the mean specific heat over the corresponding temperature range is

$$C_m = \frac{\text{Total heat absorbed}}{\pi(r_2^2 - r_1^2) D \Delta T_m} = \frac{\text{Total heat absorbed}}{(\text{Mass}) \Delta T_m}$$

In order to find the temperature range over which the calculated value of the mean specific heat is effective, the mean lower temperature may be found by integrating the initial temperature distribution by methods analogous to the above, the final mean temperature being the sum of the mean initial temperature and the mean rise computed above.

APPARATUS—A cross section of the furnace is shown in Figure 1. It will be noted that two heating elements were provided, an internal and an external. The external element was installed for the purpose of attaining steady states more readily at higher temperatures and to keep the temperature gradient in the mass small at any steady state. In connection with the internal element shunt circuits were installed for the purpose of accurately measuring voltage and current by means of a potentiometer. The same potentiometer was used for measuring the thermocouple millivoltages. All of these leads were connected to a switchboard, so that first one and then another pair of leads could be quickly connected to the potentiometer circuit. Inasmuch as the accurate meas-

urement of small millivolt differences was the important thing, it was necessary to maintain the thermocouple cold junctions precisely at 0° C. An agitator in an ice bath was used and fresh ice was added by an assistant. Both heating elements were made of chromel A wire and were wound on spirally grooved alundum cylinders, after which the grooves were filled with alundum cement. The larger alundum cylinder acted as the container for the powder. Owing to the inert nature of aluminum oxide, the thermocouple alloys selected where chromel P-alumel and no protection tubes were used except to carry the leads through the insulating material. Direct current was available at 110 and 220 volts.

ALUMINUM OXIDE—A 300-pound lot of very pure aluminum oxide was obtained from the Aluminum Company of America, through the courtesy of Francis C. Frary and Junius D. Edwards. Concerning this material Doctor Frary wrote:

This material which will be sent to you has been fused, ground, and passed through a purification process, after which it has been dried in a rotary kiln * * * The material sent you will probably contain about 99.6 per cent Al_2O_3 or perhaps a little more. The principal impurity will probably be titanium oxide in the neighborhood of 0.2 per cent. There will be a small amount of ferric oxide and traces of lime, zirconia, and silica.

A carefully sampled portion of the 300-pound lot was analyzed by A. W. Boldyreff, of the Department of Chemistry, as follows:

	Per cent
Adsorbed moisture	0.00
Chemically combined	0.00
Water loss on ignition (carbon, organic matter)	0.04
Silica	0.10
Titanium oxide	0.15
Ferric oxide	Trace
Phosphorus pentoxide	0.00
Manganese oxides	0.00
Sum of impurities	0.29
Purity of aluminum oxide	99.71
Absolute density = 3.85	

Preliminary experiments in tamping the powder showed that an apparent density of 2.28 could be duplicated as often as desired by tamping height increments of approximately 0.8 cm. each time. This procedure was followed in filling the large cylinder and the same tamping tool was used as in the preliminary tests. After packing the powder, the weight used added up to 81,542 grams and the volume filled was 35,711 cc. The mean apparent density was therefore 2.278, which checked closely with the value determined during the preliminary work.

THERMOCOUPLE CHARACTERISTICS—The wire stocks for making the chromel P-alumel thermocouples were obtained direct from the manufacturers, the Hoskins Manufacturing Company, who advised that these particular stocks were very close to their standard. This statement was verified by calibration and justified the use of their table of temperature-millivolt relations (9) as a basis for calculation. These data

were differentiated graphically (16) after finding first differences of millivolts, E , and the corresponding first differences of temperatures, T , thus giving a series of corresponding values of ΔT and ΔE . The values of ΔT were divided by corresponding values of ΔE , giving a series of values of $\Delta T/\Delta E$ covering by steps the temperature range of this investigation. These values of $\Delta T/\Delta E$ were plotted stepwise as ordinates, each value being plotted as a horizontal straight line of length ΔE , lying between the corresponding values of E , the abscissa being millivolts. Then a smooth curve was drawn through these horizontal lines in such a manner as to make the area under each segment of the curve equal to that under the corresponding horizontal line. Minor fluctuations were regarded as meaningless, but the general trend of the curve was followed faithfully, with the result shown in Figure 2. For any one pair of measurements of E from which it is desired to compute temperature rise, the mean of the two values of E is calculated and the value of dT/dE corresponding to this mean value of E is read from the curve. This value of

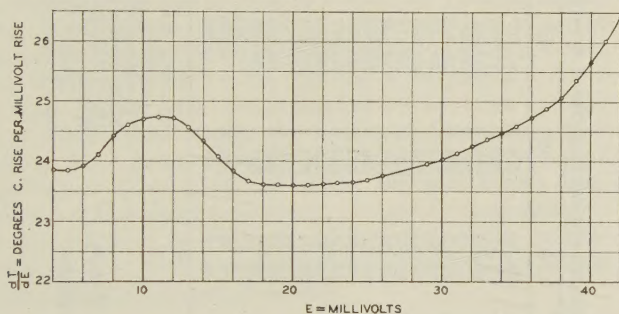


Figure 2—Electrical Characteristics of Thermocouples Used

dT/dE is then multiplied by ΔE , giving ΔT , as before indicated.

MEASUREMENTS—Twenty runs were made, each run covering a portion of the range between room temperature and 1000°C . A sample millivolt-time curve is shown in Figure 3. In general, each run required 24 hours, much of the time being required in reaching a steady state. Millivolt measurements were made while approaching a steady state and during and after each heating period. In two or three of the runs it was not expedient to wait until a perfectly steady state was reached. In those cases it was found easy to extrapolate the curves representing measurements made over a long period before the heating period in order to determine what the millivolt values would have been at the end of the heating period if no heat wave had been applied. In most cases the steady state was reached by the use of the external heating element only, so that the net heat input causing rise in temperature was due solely to the internal element.

CALCULATIONS—From the known length of wire wound on the internal core and from the total length of the core, using

Table I—Summary of Calculations of Heat Capacity of Crystalline Aluminum Oxide

A	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
1	838.62	0	838.62	11,583	29.54	274.2	41,977	7212	49,189	0.2355	111 to 145
2	849.62	0	849.62	11,737	29.15	288.0	41,926	7048	48,474	0.2421	142 to 175
3	842.11	0	842.11	11,631	28.33	248.2	40,257	6629	47,186	0.2465	173 to 206
4	817.79	0	817.79	11,295	27.72	241.2	39,395	6343	45,738	0.2470	207 to 239
5	815.81	0	815.81	11,268	27.17	235.8	38,603	6203	44,806	0.2515	225 to 256
6	821.86	0	821.86	11,331	27.54	234.1	39,130	6158	45,288	0.2507	250 to 281
7	844.73	0	844.73	11,667	27.43	225.7	38,975	5935	44,910	0.2598	312 to 343
8	826.10	0	826.10	11,410	26.83	223.4	38,118	5876	43,994	0.2594	339 to 369
9	822.72	0	822.72	11,364	25.69	214.4	36,504	5639	42,243	0.2690	375 to 404
10	819.88	0	819.88	11,324	25.57	210.2	36,339	5527	41,866	0.2705	422 to 451
11	816.95	0	816.95	11,275	25.21	211.6	35,828	5565	41,393	0.2724	462 to 491
12	826.62	0	826.62	11,417	25.28	214.4	35,917	5639	41,566	0.2747	486 to 515
13	921.05	0	921.05	12,722	28.33	228.5	40,260	6010	46,270	0.2750	526 to 558
14	906.44	0	906.44	12,520	26.31	224.3	37,384	5898	43,284	0.2892	570 to 800
15	902.83	0	902.83	12,470	26.24	222.9	37,285	5861	43,146	0.2890	621 to 651
16	912.00	37.89	874.11	12,073	25.15	209.3	35,730	5505	41,235	0.2928	674 to 703
17	922.35	42.14	880.21	12,157	24.67	201.4	35,054	5297	40,351	0.3013	705 to 733
18	233.75	16.09	217.66	3,006	5.17	95.9	7,342	2523	9,865	0.3047	706 to 803
19	307.53	29.51	278.02	3,840	6.50	101.6	9,240	2671	11,911	0.3224	806 to 904
20	294.50	37.99	256.51	3,543	6.18	80.4	8,782	2114	10,896	0.3252	905 to 973

A—Number of experimental run

I—Total measured watt-hours

II—Measured watt-hours for maintaining steady state

III—Net watt-hours causing temperature rise: I - II =

IV—Calories causing temperature rise = total heat absorbed

III × 13.812

V— ΔT_m for powdered aluminum oxide (by graphical integration)

VI— ΔT_m for aluminum core (by extrapolation and graphical integration)

VII—Mass of powder × ΔT_m for powder = $1421 \times V$

VIII—Mass of aluminum core × ΔT_m for core = $26.3 \times VI$

IX—Total (mass × ΔT_m) = VII + VIII

X— C_m = mean specific heat = total heat absorbed divided by total (mass × ΔT_m) = IV/IX = calories per gram degree

XI—Temperature range over which the mean specific heat applies (° C.)

proper corrections, it was calculated that the fraction of the total heat input effective in heating material lying between two parallel planes 1 cm. apart and perpendicular to the axis was 0.01606. Taking the equivalent of 1 watt-hour as 860 calories, multiplication of the experimental net watt-hour values by $0.01606 \times 860 = 13.812$ gives the calories effective in causing temperature rise in the imaginary disk 1 cm. thick. It can be seen that a part of the heat absorbed must have been used in raising the temperature of the internal alundum core. This rise was estimated by extrapolation of the thermocouple readings. A reasonable error in extrapolation would not be serious, owing to the very small mass of the core in comparison with that of the body of powdered material, although the small mass is somewhat compensated by the greater temperature rise in the core. The mass of alundum in 1 cm. length of the core was 26.3 grams; the mass of powder lying in the imaginary disk 1 cm. thick was 1421 grams. Inasmuch as the alundum core was composed of aluminum oxide in crystal form, the composition of the core was considered to be the same as that of the material undergoing investigation. Owing to differences in apparent density, the calculations were made on the basis of different mean temperature rises in the core and in the powder. Then the mean rise for each was multiplied by the mass and the two products added to give the total mass times mean temperature rise. In the subsequent determination of the heat capacities of other powdered solids, the now known heat capacity of aluminum oxide would be used in accounting for the heat absorbed by the core. A summary of the calculations is given in Table I, which can be understood by reference to the explanation shown therewith.

Table II—True Specific Heat of Crystalline Aluminum Oxide

TEMPERATURE	C_p	TEMPERATURE	C_p	TEMPERATURE	C_p
° K.	Cal./gram degree	° K.	Cal./gram degree	° K.	Cal./gram degree
300	0.1840	450	0.2438	900	0.2870
325	0.1975	475	0.2463	1000	0.2965
350	0.2083	500	0.2490	1100	0.3060
375	0.2213	600	0.2585	1200	0.3155
400	0.2325	700	0.2680	1300	0.3250
425	0.2400	800	0.2775		

The values of C_m for each of a long series of short temperature ranges having been computed, these values were plotted against corresponding temperature ranges and differentiated graphically in order to deduce the true specific-heat curve. Table II shows the values thus found and tabulated against absolute temperature. The values between 300° and 400° K. were obtained by interpolating between the higher values found by graphical differentiation and the lower values determined by Parks and Kelley (15).

Thermodynamic Deductions

The data required for calculating the minimum electromotive force for the decomposition of aluminum oxide into alu-

minum and gaseous oxygen at various temperatures were chosen as follows:

(a) The entropy of solid aluminum is given by Lewis and Randall (12) as 2Al : $S_{298} = 13.64$ calories per degree

The entropy of gaseous oxygen is given by Giauque and Johnston (8) as $3/2 \text{O}_2$: $S_{298} = 73.55$ calories per degree

Based upon their work at low temperatures, Parks and Kelley (15) have calculated the entropy of crystalline aluminum oxide at 298°K . Al_2O_3 : $S_{298} = 12.8$ calories per degree

(b) Moose and Parr (14) determined the heat of combustion of aluminum in a constant-volume bomb calorimeter, at room temperature.

$2\text{Al} + 3/2\text{O}_2 = \text{Al}_2\text{O}_3$; $\Delta U_{298} = -375,800$ calories. At constant pressure $\Delta H = \Delta U + P\Delta V$, and

$$\Delta H_{298} = -375,800 - 3/2 (580) = -376,670 \text{ calories}$$

(c) The heat capacity of oxygen at constant pressure over the range of temperatures from 298°K . to electrolytic cell temperature is taken from Eastman (4). The heat capacity of aluminum oxide over the same range is taken from this paper.

(d) The heat capacity of metallic aluminum from 298°K . to the melting point is taken from Eastman, Williams, and Young (5).

(e), (f), and (g). Awbery and Griffiths (1) published the following data for metallic aluminum: melting point = 657°C .; latent heat of fusion = 92.4 calories per gram; mean specific heat of liquid (657° to 757°C .) = 0.66 calorie per gram. From these values for the latent heat and the melting point,

$$2\text{Al} (\text{solid}) = 2\text{Al} (\text{liquid}); \Delta S_{330} = 5.36 \text{ calories per degree}$$

These data are utilized as follows: For change in entropy accompanying change in temperature, for a single substance,

$$S_T - S_{298} = \int_{298}^T C_p \frac{dT}{T} = 2.3 \int_{298}^T C_p d \log T$$

To the value of this integral must be added any entropy change occurring at constant temperature, such as that taking place during fusion. By plotting C_p against $\log T$ for each of the three substances, Al_2O_3 , 2Al , and $3/2\text{O}_2$, and integrating graphically over a series of small temperature ranges from 298°K . upward, the entropies of the three substances at a number of temperatures are deduced as shown in Table III. In the case of aluminum the entropy change during fusion is also shown. The column marked ΔS and the curve of Figure 4 represent the algebraic sum of entropies for the relation $2\text{Al} + 3/2\text{O}_2 = \text{Al}_2\text{O}_3$. This is a series of values of the entropy increase ΔS for the reaction $\text{Al}_2\text{O}_3 = 2\text{Al} + 3/2\text{O}_2$. For the change of ΔF in a chemical reaction occurring at constant pressure,

$$\frac{d\Delta F}{dT} = -\Delta S$$

$$\text{or } \Delta F_T = \Delta F_{298} - \int_{298}^T \Delta S \cdot dT$$

For any given temperature,

$$\Delta F = \Delta H - T\Delta S$$

and therefore at 298°K .

$$T\Delta S = 298 \times (13.64 + 73.55 - 12.8) = 22,168 \text{ calories}$$

$$\Delta F_{298} = 376,670 - 22,168 = 354,502 \text{ calories}$$

Or, rounding off

$$\Delta F_{298} = 354,500 \text{ calories}$$

Substituting this value,

$$\Delta F_T = 354,500 - \int_{298}^T \Delta S \, dT$$

it only remains to integrate the ΔS vs. T curve graphically to get a series of values of ΔF for the reaction, as a function of temperature. The deduced curve is shown in Figure 4. Changing the sign gives a series of values for the ΔF of formation of aluminum oxide from aluminum and gaseous oxygen at 1 atmosphere.

Table III—Entropies of Reaction: $\text{Al}_2\text{O}_3 = 2\text{Al} + 3/2\text{O}_2$

T	ABSOLUTE ENTROPY, S				ΔS	ΔF
	$3/2\text{O}_2$	2Al	$3/2\text{O}_2 + 2\text{Al}$	Al_2O_3		
$^{\circ}\text{K.}$						
298	73.55	13.64	87.19	12.80	74.39	354,500
330	74.76	14.97	89.73	14.95	74.78	
365	75.86	16.19	92.05	17.08	74.97	
400						346,900
403	76.96	17.43	94.39	19.38	74.91	
446	78.06	18.69	96.75	21.83	74.92	
493	79.17	19.97	99.14	24.33	74.81	339,400
500						
544	80.29	21.28	101.57	26.89	74.68	
600						331,900
602	81.41	22.61	104.02	29.50	74.52	
665	82.54	23.98	106.52	32.17	74.35	
700						324,500
735	83.65	25.39	109.04	34.90	74.14	
800						
812	84.80	26.83	111.63	37.71	73.92	317,100
898	85.96	28.32	114.28	40.60	73.68	
930	86.31	28.78	115.09	41.48	73.61	
930	86.31	34.14	120.45	41.48	78.97	307,500
992	87.12	36.62	123.74	43.58	80.16	301,900
1000						293,800
1096	88.30	40.20	128.50	46.65	81.85	
1100						
1200						285,500
1212	89.49	43.84	133.33	49.83	83.50	
1287	90.21	46.06	136.27	51.79	84.48	
1300						277,100

The minimum decomposition voltage at any temperature may then be calculated, by use of the relation

$$-\Delta F = NFE$$

in which

F = Faraday's equivalent = 23,074 calories per volt equivalent

N = number of equivalents, which, for Al_2O_3 , is 6

E = e. m. f., in volts, required to maintain equilibrium

Using the values of ΔF obtained above, and changing the sign of ΔF to indicate formation of Al_2O_3 ,

$$\text{At } 298^{\circ}\text{K.} \quad -E = 2.561 \text{ volts}$$

$$\text{At } 1223^{\circ}\text{K.} \quad -E = 2.048 \text{ volts}$$

The latter value is at a representative commercial electrolytic cell temperature, and would be the minimum electromotive

force required to deposit aluminum from a saturated solution of aluminum oxide at that temperature.

If it is desired to estimate the theoretical e. m. f. for solutions of aluminum oxide which are less than saturated, it may be roughly assumed that the activity of aluminum oxide in solution is proportional to its mol fraction, and

$$E = E_0 - \frac{RT}{NF} \ln \frac{A_0}{A} = E_0 - \frac{RT}{NF} \ln \frac{N_0}{N}$$

In the present case the solubility of aluminum oxide in cryolite at 1223° K. is about 35 mol per cent (7, 13) and, for more dilute solution,

$$E = -2.048 - \frac{RT}{NF} \ln \frac{0.35}{N} = -2.048 - 0.04045 \log \frac{0.35}{N}$$

For example, in a one-half saturated solution $N = 0.175$, and

$$E = -2.048 - (0.04045 \times 0.30103) = -2.06 \text{ volts}$$

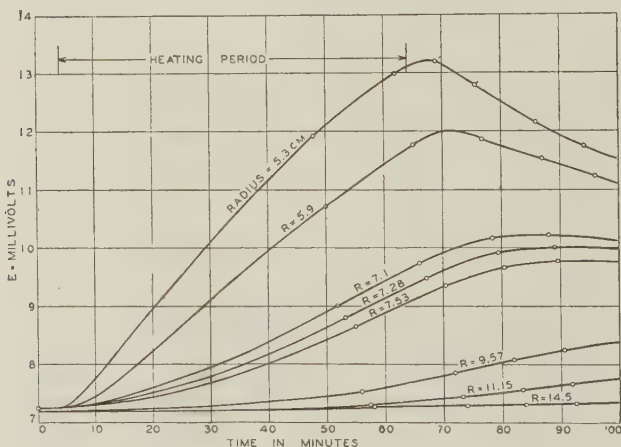


Figure 3—Sample Plot of Data Taken in Determining Specific Heat of Alumina

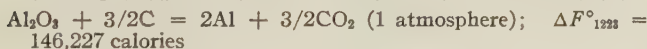
The same reasoning would apply to any variation in the composition of the solvent, as long as the solubility of aluminum oxide is known at the temperature being considered. It is to be noted that the different "degrees of ionization" in solutions of various strengths have not been considered in this calculation. It is thought probable that, at such a temperature, the aluminum oxide is almost completely ionized, and has about the same degree of ionization in all strengths of solution. If this is true, the above equation is approximately correct.

The computed values of the ΔF of formation of aluminum oxide, combined with existing data, permit the following quantitative discussion of energy relations in the commercial electrolytic aluminum cell.

The electrolyte consists of molten aluminum and sodium fluorides, which may be presumed to take no part in the cell

reactions. The cell operates with carbon anodes, oxygen being generated on the anode surface but being immediately converted into carbon monoxide and carbon dioxide with equivalent consumption of anode material. The cathode deposit is liquid metallic aluminum. It is understood that the cell operates at temperatures between 900° and 1000° C.

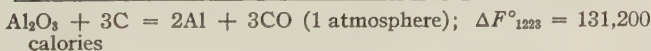
The following calculations are based upon 950° C. (1223° K.), a representative cell temperature. Eastman (3) has made a critical study of existing data concerning reactions between carbon (graphite), oxygen, carbon monoxide, and carbon dioxide. Based upon his equation for the reaction $C + CO_2 = 2 CO$, $\Delta F_{1223} = -10,016$ calories. The corresponding equilibrium constant is $K = 61.468$, and from this the equilibrium mol ratio CO/CO_2 is 0.9843/0.0157. Solving Eastman's (3) equation for $C + O_2 = CO_2$ gives $\Delta F_{1223}^\circ = -91,582$ calories. Solving his equation for $C + 1/2 O_2 = CO$ gives $\Delta F_{1223}^\circ = -50,800$ calories. From Figure 4, for the reaction $Al_2O_3 = 2Al + 3/2 O_2$, $\Delta F_{1223}^\circ = 283,600$ calories. For the reduction of Al_2O_3 by carbon, giving CO_2 at 1 atmosphere,



For the same reduction, giving carbon dioxide at 0.0157 atmosphere,

$$\Delta F_{1223} = \Delta F_{1223}^\circ + RT \ln (0.0157)^{3/2} = 146,227 - 15,154 = 131,073 \text{ calories}$$

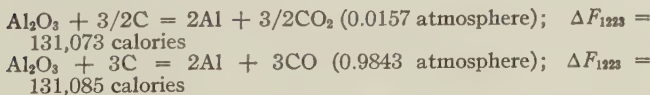
For the reduction of aluminum oxide by carbon, giving carbon-monoxide at 1 atmosphere,



For the same reduction, giving carbon monoxide at 0.9843 atmosphere,

$$\Delta F_{1223} = \Delta F_{1223}^\circ + RT \ln (0.9843)^3 = 131,200 - 115 = 131,085 \text{ calories}$$

Summarizing,



Since carbon dioxide at 0.0157 atmosphere and carbon monoxide at 0.9843 atmosphere are in equilibrium with each other in the presence of carbon, the above two values of ΔF should be identical. They would be so if the mol ratio were carried

out to a sufficient number of decimal places. Taking the average of the two values, $\Delta F_{1223} = 131,079$ calories represents the "free energy" of the reduction of aluminum oxide by carbon at 1223°K. , yielding liquid aluminum and the equilibrium mixture of carbon monoxide and carbon dioxide. The reversible voltage required to carry out this reaction will be:

$$-E = \frac{\Delta F}{nF} = \frac{131,079}{6 \times 23,074} = 0.947 \text{ volt}$$

If a commercial cell is operated at 950°C. at 6 volts and has a current efficiency of 85 per cent, the energy efficiency for the reaction in which the anode consumption is not regarded as lessening the electrical work required will be $(2.048 \times 0.85)/6 = 0.29$. This means that approximately 29 per cent of the

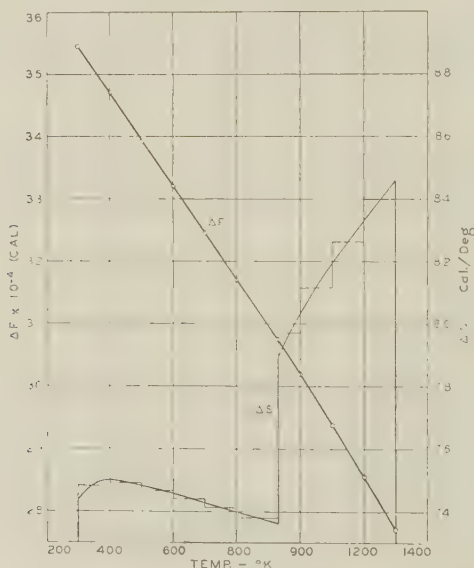


Figure 4— ΔF and ΔS for Reaction $\text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + 3/2\text{O}_2$

electrical energy input does electrochemical work, the remainder being used for overcoming resistances in the circuit and in maintaining the cell temperature. If it can be considered that the anode reactions reduce the theoretical voltage to the full extent indicated by the equilibrium values quoted above, the electrical energy efficiency will be $(0.947 \times 0.85)/6 = 0.134$, or about 13.4 per cent of the energy input is doing electrochemical work.

Edwards, Frary, and Jeffries (6), by plotting the current-voltage relation over a wide range of currents, estimate the decomposition voltage in commercial practice as about 1.7 volts. This would indicate that the anode reactions are effective in reducing the decomposition voltage. But, as is to

be expected, the actual voltage estimated at about 1.7 is considerably higher than the reversible or equilibrium voltage of about 0.95.

Acknowledgment

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Note—Since this paper was written, Droszbach [*Z. Elektrochem. angew. physik. Chem.*, **36**, 179 (1930)] has calculated the e. m. f. required to reduce aluminum oxide to liquid aluminum and gaseous oxygen at 1200° K. as 2.16 volts. His calculation was carried out in much the same manner using different and, in some cases, less reliable sources for thermal data. The following values used by Droszbach may be compared with those given in Table III:

	ABSOLUTE ENTROPY	
	273° K.	1200° K.
2Al	...	36.6
3/2O ₂	72	87.75
Al ₂ O ₃	16.8	52.8

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